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THE PRESENT STATE AND DEVELOPMENT PROSPECTS
OF INORGANIC AND PHYSICAL CHEMISTRY IN POLAND

It passed 11 years since 1948 when the first post-war Congress of the Polish Chemical Society was held in Wrocław. After the war time, so tragic for the Polish science, there met chemists to review their first scanty results of work which they have just resumed.

The present Jubilee Congress coincides with the 15th anniversary of restoration of the new social order in Poland. This is a sufficiently long period for the chemical sciences being in dynamical development as to make an account of its progress and achievements as well as to present an outlook for its further development. However, it is not possible to deal with chemistry as a whole in one lecture. Therefore I had to restrict the subject to two basic branches which are inorganic and physical chemistry only - without analytical and applied chemistry - and even in these topics just to the more important achievements.

In the period of 1919 - 1939 several outstanding chemists acted in this field. Majority of them, like Jabłozyński, Zawadzki, Szyszkowski, Centnerszwer, Glixelli, Tołłoczko, Ekasko, Bekier, and recently Miłobędzki are no longer alive. In many cases also most of their co-workers met their death during the war time. Thus in 1945 the situation in Polish

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chemistry was extremely difficult.

Despite those losses, when comparing the pre-war 20 years' period with the last 15 years, a striking progress is observed: the base for development of fundamental chemical research has been considerably enlarged as well at Universities and Technological Institutes where the number of Chairs has been at least doubled, as in the Polish Academy of Sciences where a new Institute of Physical Chemistry has been created. Thus the number of the research staff increased several times. In that new period their activity in physical and analytical chemistry was also evident from several meetings, like the Electrochemical /1955/, Polarographical /1956/, Chromatographical, and recently the meeting devoted to kinetics and chemical catalysis /1958/.

To present the results of our researches it was necessary to analyse a great number of publications, which only in "Roczniki Chemii" and the Bulletin of Polish Academy of Sciences amounts to 700 papers, and to arrange them accordingly to definite sections. To start with I am going to speak about the chemical syntheses.

In this branch the fundamental researches in chemistry of phosphorus were continued by Mikobędzki and Kolutowska /Warsaw/. They dealt with: 1/ condensation of phosphoric acid into hypophosphoric acid, finding thereby that it can be formed only through the unstable α -form of phosphoric acid. This is because the α -form can be easily deelectronized while the β -form has very stable tetracoordinative saturation of the central phosphorus atom, 2/ condensation of orthophosphates into pyrophosphates, 3/ pyrolysis of hypophosphate $/Na_2H_2P_2O_6/$ into hypophosphite $/Na_2H_2P_2O_5/$. The course of these processes was explained by homolysis, i.e. by the mechanism of radical decomposition of molecules of a chemical compound. Similar mechanism was given as well for autoredoxidation of sodium hypophosphite $/NaH_2PO_2/$.

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metabisulphite $/Na_2S_2O_5/$ as for explanation of the oxidizing action of sodium hydroxide on hypophosphite which then releases hydrogen and forms phosphite $/Wieczffinski - Warsaw/$.

Systematical researches on the synthesis and the chemical and physical properties of mixed ethyl-phenyl esters of orthosilicic acid were carried on by Rodziewicz $/Gdańsk/$, who described - among others - a new method of their synthesis in the gaseous phase. He succeeded in obtaining some further esters of this acid with a third-order alcohol containing three chlorine atoms, so called chloroethon. As well there was elaborated a method depending on introduction of one to three isothiocyanate groups into phenoxysilane. The substances mentioned above are of great importance for impregnation of materials, making them waterproof.

There have been elaborated new methods of synthesis, like a/ the preparation of ferrites which because of their magnetic properties are of great practical importance $/Krauze and Wolski - Poznań/$, b/ synthesis of inorganic pigments $/Kranz - Poznań/$, and c/ synthesis of series of thallates of various metals, whereby the amphoteric character of thallium $/III/$ was proved $/Kapitańczyk - Poznań/$.

A new simple method, depending on the reduction of permanganate in the melt with NaOH, allowed to obtain sodium hypomanganate Na_3MnO_4 , a compound of Mn $/V/$ $/E. Jeżowska-Trzebiatowska - Wrocław/$. As well the investigations on the complex compounds were developed there, firstly with rhenium and then with vanadium and uranium, whereby numerous new compounds of these elements were obtained. Among others a compound of monovalent $+1/$ rhenium was stabilized in the complex with dipiridyle. Many of the obtained complexes, particularly mono- and poly-nuclear, have been the subject of detailed structural researches what will be mentioned later on. At this place also a new method of growing crystals of tertiary heavy metal phosphates may be noted $/W. Hubicki - Lublin/$.

The problems of the structure of inorganic compounds have developed in Poland in much higher degree than the synthesis of inorganic compounds. The variety of problems was considerable and the applied re-

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search methods manifold.

The problems regarding the structure of chemical compounds have a wide aspect. They may be solved by the classical analytical procedure. On the other hand here belong the determinations of structure of chemical compounds by methods of X-ray analysis, ~~further the determination of~~ electronic structure of molecules and solids due to their magnetic, electric and optical properties, the determinations of dipol momenta, and other methods which may be applied also for determination of the structure of ions in solutions.

In all these branches we may note a pronounced progress and considerable achievements.

Let us start with the structure of simple compounds, and then of the complex ones.

The X-ray analysis used for determinations of unknown structures of chemical compounds and giving atom coordinates as well as their coordination within the unit cell has been developed in Wrocław and Łódź. The structure of some metallic compounds of rhodium and zirconium has been solved by W.Trzebiatowski and K.Łukaszewicz. Systematic determinations of structures of alkaline earths titanates were carried out /K.Łukaszewicz/ by applying the methods of projections of electronic densities deduced from the Fourier and Patterson synthesis. In the Department of Inorganic Chemistry of the Institute of Technology, Łódź, the structure of iodo- and bromo-diarsenite was determined /Z.Gałdecki/. In Wrocław the magnetochemical investigations and electrical conductivity methods have been developed /W.Trzebiatowski, B.Staliński/. They examined systematically the hydrides of some transition metals like uranium, lanthanum, cerium and others which hitherto have not been investigated by these methods. Among others the ferromagnetic properties of uranium hydride, deuteride and telluride have been found, such magnetic properties being discovered in the actinium series for the first time. To the contrary of the metallic conductivity of uranium hydride the lanthanide hydrides /of lanthanum and cerium/ show the properties of semiconductors which have been determined, and what proves that they form intermediate compounds between metallic and salt-like ones.

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A similar behaviour was found with silver hypofluoride $/Ag_2F/$ for which the electrical conductivity and the Hall effect have been determined, thus enabling to define the type of the current carriers.

Further semiconducting properties of chemical compounds have been investigated on the example of barium titanate $/Pigon - Wrocław/$ which shows intrinsic conductivity at low temperatures, as well as on some intermetallic compounds like zinc and cadmium arsenides $/W.Trzebiatowski/$. All these researches were carried out by employing a complete equipment for different physical methods including the determination of Hall effect within wide temperature range and using monocrystalline samples purified by the zone-melting method.

The researches on the electrical conductivity of some organic derivatives of dihydroxybenzene, like methylene blue, have been initiated by prof. Gumiński $/Wrocław/$. Later on the investigations on the resorcin were continued in Cracow where some attempts were undertaken as to broaden the theoretical elaboration of the conductivity mechanism from the point of view of so called metallic model $/A.Gołębiowski/$. As it is known the determination of some optical properties - such like absorption spectrum - is very useful for the description of the electronic state of solids in terms of band theory. So in case of dihydroxybenzene the optical researches supplemented the electrical conductivity measurement.

The works on chemiluminescence must be included into the mentioned branch of chemistry. The mechanism of chemiluminescence of lucigenin under the action of H_2O_2 and its oxidation kinetics was investigated by Kroh $/Łódź/$ as well as the chemiluminescence mechanism of luminol in the presence of catalytic acting agents.

Analogical problems of the kinetics and phosphorescence spectrum were elaborated on the example of thallium activated potassium bromide. The investigations on the light emission of the oxyd layers on aluminium anodes and their photoluminescence enabled to draw a conclusion, qualifying the observed phenomenon as the electroluminescence effect $/K.Gumiński and Z.Ruziewicz - Wrocław/$.

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On the basis of absorption spectrum, photoelectrical conductivity and some thermoelectric properties of KCl crystals activated with metallic thallium /phosphor/ full particulars of electronic structure were given, explaining the character of the current carriers and proposing an adequate band model together with the schemes of electronic transitions /Rohleder - Wrocław/.

The structure of carbonylcyanide -CO/CN/_2^- , obtained for the first time by Małachowski in Lwów, was determined on the basis of absorption spectrum, as well as its force constants were calculated /Tramer - Warsaw/.

Essential information concerning the structure of molecules can be obtained by measuring their dipol momenta. This research methodics was developed by J. Hurwic /Warsaw/ who introduced some simplifications by adopting in place of troublesome anhydrous solvents the saturated water solutions in benzene. This way he examined - among others - the tautomerism of -aminovinylketone.

The measurements of dielectric polarisation helped to appreciate the molecular interaction of different organic compounds, particularly with respect to hydrogen bond. As well there was elaborated a general classification of different types of hydrogen bonds /L. Sobczyk - Wrocław/.

Similar investigations on the structure of complex compounds deserve a separate treatment.

W. and Z. Jakób /Cracow/ presented interesting results pointing on the existance of complex compounds with coordination number 10 on the example of molybdenum and tungsten /IV/ cyanides which are able to coordinate to the present 8 cyanide groups two non-cyanide ones, for example those of H_2O , NH_3 , N_2H_4 . The said W. Jakób proposed for another molybdenum cyanide /so called Heide-Hoffman salt/ a new binuclear coordination formula. Studying the structure of the binuclear cobaltammon complex he found it to constitute a stable redox-system containing the negative O_2^- bridge. Besides, Swinarski /Toruń/ obtained several selenium-cyano-mercurates of heavy metals, at the same time determining their solubilities.

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The Wrocław School /E. Jeżowska-Trzebiatowska/ has carried out researches on the structure and chemical bond of poly-nuclear complexes and their magnetic properties. A new group of diamagnetic bi-nuclear rhenium /IV/ complexes was discovered and the role of the oxygen bridge in formation of these complexes from single paramagnetic Re/IV/ ions was proved, indicating a kind of internal molecular antiferromagnetism. Another kind of diamagnetism was detected in rhenium /V/ complexes which have been proved to be mono-nuclear. In this case the diamagnetism was explained by applying the crystalline field theory, what enabled the determination of degeneration of energetic levels of d-electrons. On the example of vanadium /III/ complexes there was elaborated the first genuine method of real stoichiometric coefficients determination for poly-nuclear complexes formation, as well as the method for calculation of the stability constants of poly-nuclear complexes /L. Pajdowski - Wrocław/.

It has been proved that one of the bi-nuclear rhenium /IV/ complexes, i.e. the μ -oxo-oxo-chlororhenate has the properties of inorganic ferment and thus the ability of the reversible oxygen binding. The function of an intermediate complex was established, and as it was proved, the absorption of one oxygen atom occurs through the oxygen bridge turning into peroxygen one. Applying radiochlorine exchange the difference in chlorine bonding between the chlororhenates and chloroplatinates was stated.

A considerable number of works was devoted to the structure of complex ions in solutions in connection with solvation and complex formation in water and organic solvents, generally applying optical methods. Among others, copper and cobalt compounds in water and aliphatic alcohols were the subject of St. Minc's works. There were measured the configurational equilibria between 6- and 4-coordinative ions of cobalt /II/ in aqueous solutions containing neutral salts /W. Libuś/, what enabled to draw some conclusions on the influence of ionic force on the mentioned equilibria. Comprehensive study on the solvation and complex formation of uranyl nitrate in organic solvents of wide range of dielectric constants were

carried out in Wrocław /B. Jeżowska-Trzebiatowska/, applying the analysis of absorption spectrum. In this study the ionisation of the compound in question was determined by measuring the electrical conductivity and hence calculating the dissociation constants of ionic pairs and triplets. There was separated and determined the structure of the uranium nitrate complex with TBP.

The solubility product of the whole series of heavy metals ferrocyanides like those of Cd, Co and Cu were determined by various methods /A. Basiński - Toruń/ and the formation equilibria for rhodano-mercurate, among others in acetone and ethyl alcohol, were examined by A. Swinarski /Toruń/.

The distribution equilibria of a chemical compound in the liquid-liquid system possess essential meaning for analytical purposes, and also for purification of chemical compounds. This subject was elaborated by M. Kemula /Warsaw/. He derived theoretical dependences enabling to establish the conditions of distribution between non-miscible liquids, among others by adding a third component soluble in one of them. Then he extended it to the distribution law for acids and alkalies.

Some assumptions concerning the extraction theory of uranium compounds were elaborated by St. Fine and Libuś /Warsaw/ as well. Not all chemical processes occurring in solutions are dealing with complex formation or reactions. Interesting results about the mechanism of heavy metal phosphate precipitation have been obtained by electronic ^{methods} by W. Hubicki /Lublin/ who stated their hydrolytic behaviour. Investigating the precipitation of lanthanum phosphate with di- or tri-sodium phosphate he found hereby that in spite of adding an alkaline solution to the previously acidic solution of the lanthanum salt the acidity of resultant solution increases, what has found its explanation in water chemisorption on the precipitate and following acidic dissociation of the basic phosphate.

The tautomeric equilibria of nitric acid in relation to the medium have been the subject of the researches of Raman

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spectrum /line - Warsaw/. The influence of the solution acidity on the polarity of the HO-NO_2 bond was found. Hence the opinion was expressed that in acidic medium not only the NO_2^+ ion but also undissociated molecule may act as a nitrifying agent. The investigation procedure was improved as well whereby an objective method of intensity determination of Raman lines was elaborated, considering the influence of different experimental conditions /Kęcki - Warsaw/. It was later applied in the researches on the intermolecular action of dissolved salts on the solvent, e.g. for ZnCl_2 and CaCl_2 in methanole. The properties of nitric acid - sulphuric acid system have been the subject of researches of A. Swinarski /Torun/. Basing on the viscosity and electrical conductivity measurements in the system there were detected compounds and ionic forms allowing the author to undertake an attempt to reconcile the opinions of Hantsch and Ingold.

Also in the field of the chemical bond theory in terms of quantum mechanics we have to note the first papers. Kokos /Warsaw/ calculated the Coulomb interaction integrals of electrons in atom thus introducing essential correction to the theory of molecular orbitals and improving the calculations of energy levels of molecules, applying it to ethylene and benzene molecules. Considerations on applying a free electron model of metals to a free atom as well as calculations of energy of organic molecules were done by Gołębiowski /Cracow/ who derived also a three dimensional model of σ and π electrons for organic particles.

The model of free electron was used also by Kokos for d-electrons of metallic ions what, in connection with crystal-line field theory in which energetical levels undergo splitting, allowed to calculate the excitation energy of ions, and later on to explain the structure of absorption spectrum of some complex ions.

The chemical individual is not only characterised by its qualitative and quantitative composition, thermodynamical properties and structure, but also by its attitude towards other individuals in establishing - among others - some phase

equilibria in binary and poly-component systems, sometimes in wide temperature or pressure ranges.

In the branch of phase equilibria of organic compounds like liquid-vapour and liquid-solid systems the School of prof. Świętosławski /Warsaw/ is traditionally dominating. The achievements of this School are especially of great importance because they are directly connected with one of the most important branches of our new national industry, i.e., further recast of the products of dry distillation of coal. Even a superficial survey of numerous works and achievements of prof. Świętosławski and his School calls for a separate lecture as in the post-war period the development of this branch is expressed by a large number of publications /over 270/ in which several co-workers like K. Zięborak, W. Łaleśiński, A. Orshag, T. Penkala, A. Bylicki, Stecki, Kręglowski and many others have their contribution.

The majority of works deal with azeotropic extended on 3-, 4- and more component systems whereby some new types of 3-component azeotropes as well as homo- and heteroazeotropy of quaternary systems were discovered on numerous examples. These systematical researches were carried with the homological series of organic compounds. Basing on these researches a full classification and terminology for hetero- and homoazeotropes was given and presented to the IUPAC as a project of international classification.

In researches on composed polyazeotropic mixtures like coal tar and other organic raw products he introduced the conception of the main component which is of essential importance for such systems. The methodics and experimental technics for the examination of polyazeotropic mixtures has been developed determining the possibility of formation of azeotropes revealed. The experiments have been accomplished by theoretical works establishing thermodynamical foundations and relations, e.g. between the composition and azeotropic depression, treating the azeotropes as regular solutions. On this basis the properties of azeotropes can be foreseen.

Numerous phase equilibria of organic compounds have been examined under an increased pressure especially in the critical temperature range. It has been found that critical temperatures of binary and ternary azeotropes deviate - sometimes considerably - from the Pawlewski's rule, since azeotropes appear also in criti-

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cal state. There were investigated the phenomena of pre- and post-critical range with use of a new method, as well as the factors determining the limited mutual stability of compressed gases.

For experiments on liquid-solid equilibria new types of cryometers were designed. According to Świętosławski the freezing point of the main crystallization component for so called ideal eutectic system depends only on its molar fraction in the solution. This rule has been checked on many experiments as well as the dependence function of these two factors for ternary eutectics was deduced. Then this rule was transferred on eutectics of ionic compounds /salts/ and on their transitions into solid solutions.

Further works from the branch of calorimetry will be spoken about later. However, I do not discuss here the works connected with the application of these fundamental researches in practice, as they are to be dealt with in a separate lecture of the author himself.

To the branch of phase equilibria of condensed systems belong metallic alloys and oxide systems. In the Wrocław School /W.Trzobiowski and J.Borak/ there have been elaborated the phase diagrams of binary titanium-copper and rhenium-platinum systems. Investigations on appearing of so called δ -phases in binary and ternary alloys of rhenium with different transition metals as tungsten, molybdenum, niobium, tantalum and the like were carried out /J.Niemiec/. There have been elaborated phase diagrams of binary systems of titanium dioxide with the oxides of the second group metals like BeO, BaO and SrO /M.Dryś/. These investigations required overcoming the difficult high-temperature technics, as the melting temperatures exceed here 2000°C . Furthermore phase diagrams were elaborated for ternary systems of $\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$ and binary $\text{MgO}-\text{P}_2\text{O}_5$ important for the fertilizer industry /J.Borak and J.Wojciechowska - Wrocław/. Similar works on the $\text{CaO}-\text{MgO}-\text{P}_2\text{O}_5$ were carried out by W.Bobrownicki and co-workers /Wrocław/

The phase equilibria are conditioned - as it is known - by thermodynamical potentials of the components of the system. Thermodynamical functions of pure components, as well as those of chemical processes, may be determined in different ways.

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To the classic methods belongs calorimetry which in Poland has its tradition in the School of prof. W. Świętosławski and A. Dorabialska. A series of works in this branch were carried out by prof. Dorabialska and Łażniowski /Łódź/. Among others there was determined the solubility heat of langbeinite, and the heats of allotropic transitions of selenium and sulphur. The micro-calorimetric methodics was extended by Łażniowski who elaborated dynamic determination methods of short-lasting variable heat effects and determined by this method the enolisation heat of β -bi-ketones. In prof. Świętosławski's laboratory a new type of labyrinth calorimeter was constructed for measurements of small and long-lasting heat effects, e.g. of metallic alloys, binding process of cement etc. By the way let me announce that B. Staliński /Wrocław/ has constructed a low-temperature calorimeter for the temperature range of liquid hydrogen, the liquefaction of which has been overcome as well.

In convenient circumstances the thermodynamical properties may be determined electrochemically by the measurements of electromotive forces, namely by measuring them in the wide temperature range. This method was used in our laboratory /W. Trzebiatowski and J. Terpiłowski - Wrocław/ for determination of the basic thermodynamical functions of metallic alloys in the temperature range up to 800°C. These works were undertaken to demonstrate essential differences at the course of fundamental thermodynamic functions between intermetallic phases of variable composition, which are called berthollides and dalthonides. Then these works were extended on liquid alloys of indium with other metals, thus characterizing the solution types of liquid metals.

Now there should be mentioned the works on certain anomalies occurring in the values of vapour pressure in the solvent-salt-organic compound systems which have found the explanation by a semi-empirical theory /Sarnowski and Baranowski/.

In several publications Baranowski /Cracow-Warsaw/ dealt with electrothermodiffusion applying new, elaborated by himself thermodiffusional method for the solvents, which may be used for determination of Soret coefficients. Baranowski has

given the theory of this method basing on thermodynamics of irreversible processes which he also applied to some migration taking place in liquid metallic alloys under action of the electric field.

Now I would like to discuss the electrical phenomena occurring at the interface between two phases, a branch of physical chemistry being developed by the School of prof. Kamieński /Cracow/ and then by prof. Waksmundzki /Lublin/. The works have been developed here in three directions, namely:

- 1/ surface electric potential of solutions
- 2/ absorption microcell and its application
- 3/ phenomena accompanying the flotation processes

Within the first direction, which is particularly important in understanding of biological processes and experimentally belongs to extremely difficult ones, the influence of numerous substances on the surface electric potential of aqueous solutions was established. There has been discovered a new rule connecting the dissociation constant of the given substance with the surface tension and electrical potential on the surface of the solution. Among others it was shown that there exist some substances raising the interfacial potential. Here belong those containing in a molecule the hydrophilic and a negative dipol groups being set apart at sufficiently far distance in the "para" position. At the close position /e.g. "ortho"/ due to the different orientation of the molecule the potential decreases. These researches enable to estimate the normal surface electrical potential of pure water which equals about 1 V with the negative field directed towards the air. In nearly 100 publications genuine absorption micro-cells /constructed by prof. Kamieński/ have been described as well as their applications. The cell of this type presents an extremely sensitive instrument helping to detect all electro-chemically active substances as well of basic-acidic character as of oxidant in aqueous and non-aqueous solutions, and in the gaseous phase. The cell has found various applications within the potentiometric absorption analysis, e.g. for the control of the outflow from chromatographic columns as well

as a detector in the paper electrophoresis and a detector of chemically active gases in the air. Its sensitivity is so high that the amount of $7 \cdot 10^{-6}\%$ of chlorine in the air causes the change of the electrode potential of 50 mV. On elaborating the physical-chemical problems of such a complicated process like the flotation the measurements have been made as well of the total potential difference on the interface as in the diffusional part of double electric layer, what in several cases enabled to explain the phenomena accompanying the flotation process.

In connection with the surface phenomena it is convenient to present now the works dealing with colloid chemistry, being unfortunately rather undeveloped in this country, for only a small number of papers has appeared on this topic. There are to be mentioned here the works of W. Wójciak from the School of prof. Gałęcki /Poznań/ concerning the physical-chemical properties of copper and Paal-gold hydrosols for which the colour, viscosity, electrical conductivity and electrokinetical potential were measured in dependence on protective colloid contents, the age and irradiation time. To the same branch belong the works of Basiński and Basińska /Toruń/ on the preparation of hydrosols and hydroxides of Al, Cr and Fe on the ionic exchange resins, further the investigations on coagulation, stability and light absorption for silver halogenides and finally those of formation mechanism of molybdenic acid hydrosols.

Researches in electrochemistry have been continued by a number of Departments and Institutes. They concerned the mechanism of electrode processes with adjective phenomena and in a broad range the polarography. To the first mentioned field belong the investigations of the late Kamecki and Zembura /Cracow/ devoted to anodic dissolution of copper, zinc, iron and lead in different acids, alcalies and salts by determining the polarisation curves. Some phenomena occurring during the passivation and essential for the anodic polishing processes could be explained. Similar works were carried out by the mentioned authors on the mechanism of precipitation of metals from the solution.

Other aspects of electrochemistry are represented in the works of Smiałowski and Szklarska-Smiałowska /Warsaw/ who developed some theoretical background of corrosion processes important in technology. Among others they have followed the diffusion of hydrogen into iron and nickel cathodes taking the advantage of the marked dilatational effect resulting from high pressures of hydrogen, especially in its atomic form. Detailed investigations of these effects enabled the appreciation of the pressures as well as the calculation of diffusion coefficients of hydrogen from its desorption velocity from the oversaturated cathode. It was found that the presence of some catalytic poisons impairing the hydrogen recombination effects markedly the dilatation increase, thus enabling to arrange these poisons accordingly to their activities and to explain the low hydrogen overpotential on iron. For the first time the curves of cathodic polarization were investigated on different planes of large iron monocrystals, throwing thus a new light on the intercrystalline corrosion mechanism because in ammonium nitrate solution the potential differences between the planes reach the value of 0.5 V. With the same method there was found that the corrosion in ammonium nitrate solutions may be effectively impaired by the presence of fatty acids, the action of which depends on the length of the hydrocarbon chain.

The dependence of hydrogen overpotential on the kind of the solvent was the subject of investigations of St. Janc /Warsaw/, whereby the relation between the overpressure from the one side and the solvation energy of hydrogen ion and the polarizability of solvent molecules on the other hand has been established.

Further on there should be mentioned the first works on the cathodic processes which were carried out for the electrolysis of fused calcium and sodium salts. Some explanations of the formation of sub-ions were given here /L. Suski-Cracow/.

The polarography is the last branch of electrochemistry which is to be presented here. In Poland the leading part in this field is played by prof. Komula and his School /Warsaw/. Because of extensive range of their

works I must restrict myself to some most important achievements, especially to those having the essential influence on the development of analytical methods, or being of fundamental importance for the processes on the dropping electrode.

First of all there belongs here the elaboration of detailed theory of concealed limiting currents, what was of very importance in application of polarography to the problems of quantitative analysis. Among others the damping effect of the diffusional currents by metallic hydroxides was explained as well.

In the mentioned School polarography was utilised in researches on reduction mechanisms and kinetics of organic and inorganic compounds, including the complex ones. In many cases it was possible to draw some conclusions on the existence of tautomerism, e.g. in p-hydroxybenzaldehyde, to connect the course of polarography curves with different chemical properties, even with those of stereoisomers, and to show the most subtle details of the reduction mechanism of complex compounds depending on their structures, e.g. in some cyanide complexes /Sickierski - Warsaw/. Similarly the influence of surficially active substances /like non-polar compounds/ on polarographic waves was proved.

Particularly rich achievements in respect to chemical analysis was obtained by combination of polarographical method with chromatography. After the final improvements the chromatopolarography enables for instance the quantitative separation within the series of aliphatic homologues of nitro-compounds or among the isomers of nitro-aromatic ones. Recently prof. Kemula elaborated the principle of a new so called "hanging" electrode which is in shape of a motionless mercury drop. In this way a pronounced sensitisation of the polarographic method, which is said to reach 100,000, was enhanced due to the cumulation of the trace-amounts of metallic ions from the solution. Thus it was possible to detect the unstable intermediate products, for example in the reaction of the reduction of nitrobenzene, and some intermetallic compounds formed in mercury.

Using the polarographic methods it was possible to show that the reduction of rhenium cyanide complexes leads to +1 and even -1 valence numbers for rhenium, and to obtain some information on the mechanism of reduction of Fe and Mn oxyanions /B.Jeżowska-Trzebiatowska and Biernat - Wrocław/.

An interesting application of polarography at low temperatures may be noted as well. There were applied new solvents like liquid ammoniakates composed from nitrates and iodides of lithium, ammonium etc. /W.Hubicki - Lublin/. These compounds form quite satisfactory solvents even from such substances like carbonates, sulphates and fluorides being thereby good conductors of electricity. Different polarographic determination have been carried out for the solutions of these salts.

In the field of methodologies there must be mentioned another new method of differential rapid-running polarography /Goerlich - Cracow/. Finally there should be mentioned the works on some applications of dropping mercury electrode, which was used by Mine /Warsaw/ for measurements of the capacity of double layer. The author determined the influence of polarisability of cations on the differential capacity, its dependance on dielectric constant of the solvent, and the influence of the solvent itself on the desorption potentials of the halogenide acids.

The kinetics of chemical processes belongs to another traditional branches of chemistry being still developed in Poland. Its application to the solutions constitutes the main problem of the researches carried out by prof. L. Józefowicz /Łódź/. His works concern the kinetics of chemical processes in binary phasic systems on the interface between liquid-liquid or liquid-gas phases. Here belong investigations on the kinetics of the reaction of arsenious acid or sulphur dioxide with iodine on the interface of water-organic solvent /St.Witekowa/. In the first reaction the deciding step is initiated by the reaction between atomic iodine and molecules of arsenious acid, while in the second one an unstable complex of the formula $\text{SO}_2\cdot\text{HI}$ is formed. Hydrolysis of sulphuryl sulphide dissolved in CCl_4

was examined on the interface with aqueous phase with changing pH whereby there was found that the velocity of the reaction is markedly enhanced by the addition of substances lowering the surface tension, what points on the deciding significance of absorption.

The kinetics of the reduction reaction of iron /III/ salts by means of tin /II/ ions was examined in terms of the contents of different neutral salts in the solution A.Ulińska - Toruń/.

The kinetics and mechanism of ox-red reactions have been the subject of the researches of B.Jeżowska-Trzebiatowska and co-workers. The investigations on the reactions between the ions of the same sign have been of particular interest. There were examined the reduction processes of metallic oxy-anions by hydroxy ions $/OH^-/$ and disproportionation reactions of the oxy ions. For the first time there was proved the multistage course of reduction of permanganate to Mn /IV/ and its varying mechanism depending on the concentration of the alkali. Independently the reduction and decomposition processes of ferrates /Fe-VI/ have been examined here /I.Wronska/.

To explain the course of the reaction of a technologically important process, the work on oxidation kinetics of nitrosylsulphuric acid under the pressure of oxygen up to 100 at. were undertaken by St.Bretsznyder /Warsaw/. This enabled him to conclude that under high pressures the oxidation of niter takes place mainly in liquid phase. Similar aspects had the investigations of Bretsznyder on the hydrolysis of aluminium sulphate solutions being under pressure, as well as on the kinetics of oxidation of SO_2 contained in these solutions by means of dissolved oxygen. It was proved that the reaction proceeds by two parallel mechanisms, i.e. chain and catalytic one, whereby the former predominates in diluted solutions while the latter in concentrated ones. Also the way of interaction between SO_2 and ferrous ions contained in solutions was kinetically examined and the origin of the colours appearing here was explained by complex compounds formation.

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In solutions there were investigated several polymerisation reactions, e.g. of methylmetacrylate by means of absorption spectrum in u-v range /Kroh - Łódź/, photopolymerisation of vinyl bromide /Kryszewski - Toruń/, and photopolymerisation of acetic aldehyde /Wojteczak - Poznań/.

Decomposition kinetics of organic compounds was examined on the example of decarboxylation of picoline, nicotine and lutidine acids /A. Bylicki - Warsaw/.

The kinetics of gaseous reactions was elaborated by J. Zawadzki /Warsaw/ on example of Boudouard's reaction. To this branch belong the works of St. Ciborowski /Warsaw/ on hydrogenation of acetone to propyl alcohol the kinetics of which, as well as equilibrium in gaseous phase, has been established in presence of catalysts.

Investigations on kinetics of carbonates dissociation were carried on by Zawadzki and Bretsznayder /Warsaw/. Zawadzki examined the decomposition of zinc carbonate under various pressures of CO_2 finding thereby that the true equilibria are not established. In this case the activation heat is higher than that of the reaction and hence the temperature is of great influence.

Bretsznayder continued his works on the dissociation mechanism of solids. He proved that in ranges considerably distant from equilibrium state the velocity of nuclei formation of new phase on the interface determines the dissociation kinetics. Accepting the Langmuir's assumptions he derived an equation establishing the dependence of nucleation velocity on the oversaturation degree. The value of activation energy inversely proportional to the square of the oversaturation logarithm proved that the velocity of formation of new centres depends in the same way on the oversaturation as the velocity of formation of new phase in condensation, boiling or crystallisation processes.

Investigations on the mechanism of chemical reactions in the solid state were carried on in Wrocław, too /W. Trzebiatowski, J. Damm and J. Wojciechowska/. There was determined the detailed course of such reactions like synthesis of technically important metatitanates of barium and strontium

and the decomposition reaction of anhydride in the presence of quartz by establishing intermediate products and partial reactions.

In Cracow A. Bielański followed the course of synthesis of several spinels from their oxide components - typical semiconductors - applying the measurements of electrical conductivity in dependence on temperature and oxygen pressure what revealed the complicated character of the process starting already at the temperature of 200 - 300°C.

To the discussed branch of chemical reaction in solid state belong the works of L. Czerski and his co-workers /Cracow/ on the topology of oxide or sulphide layer formation on pure metals or alloys. By applying the technics of built-in "indicator" in shape of thin platinum wire the authors could distinguish two differing layers and determine the mechanism of their formation in terms of diffusion of metallic ions and electrons. The velocity of the reaction is determined by the diffusion of metal through the layer according to the parabolic law. There was investigated the oxidation kinetics of copper /I/ oxide whereby it was demonstrated that the increase of the oxide layer is caused by the diffusion of oxygen through its lattice.

The catalysis phenomena are closely connected with kinetics but the heterogenic catalysis offers a different specification being connected with surface phenomena and the electronic and crystalline structure of the contact. As the contact catalysts are of great importance for the chemical industry the researches in this branch are particularly essential, although they are rather complicated. The works in this branch were initiated by J. Zawadzki /Warsaw/ who examined the mechanism of ammonia decomposition on iron by statical and dynamical methods and stated the first-order reaction.

Another extensive work of Zawadzki concerned the ammonia oxidation on platinum. He presented the radical mechanism for this process, finding on the base of kinetical measurements and identification of some intermediate products that nearly every ammonia molecule coming in touch with platinum surface reacts into NO. This high efficiency depends

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on the velocity of several partial reactions in which the formation of imide radical $/-NH/$ from NH_3 and atomic oxygen is - according to Zawadzki - of deciding importance. It would have been very appropriate if Zawadzki's inventive works and theory found followers in this country.

Basic works on the heterogenic catalysis have been developed in Poland subsequently in University centres of Poznań, Cracow, Gliwice and Wrocław. They have been undertaken with respect to different points of view on the contact structure. The School of prof. A. Krauze /Poznań/ in numerous works continued researches on catalytic activity of amorphous oxides with traces of heavy metals ions deposited on them. Applying some standart methods like decomposition of hydrogen peroxide, oxidation of indigo-carmin etc., the specific character of catalytic activity has been sufficiently explained for binary or multi-component contacts in dependence on their qualitative and quantitative composition. There were found and described various specifical features of adsorbed ions which have been denominated as ionic "synergism", "double-face character" of the carrier, catalytic mutation, and others. There were presented examples of extremely high activity of catalysts so called inorganic superferments.

On this foundation, and basing on his own opinions on the radical structure of hydroxides the author described several mechanisms for catalyzed reactions.

Chemical changes of vanadium catalyst, taking place during oxidation of SO_2 and resulting in formation of vanadyl sulphate were the subject of Weychert's /Warsaw/ thermogravimetical investigations in which he stated very high velocities of formation of this compound.

Researches on the electronic factor of oxide and metallic catalysts were carried out by two methods, namely the electrical conductivity /A. Bielański - Cracow/ and the measurements of magnetic properties /W. Trzebiatowski - Wrocław/. In the former case the process of dehydrogenation of alcohols and its influence on the electrical conductivity of mixed oxides were the subject of numerous researches. Several regularities were found here, for instance that the conductivity of the oxi-

des of n-type increases while that of the p-type decreases. These changes are parallel with the effectiveness of catalytic reaction, what in some cases was possible to be expressed by a mathematical dependence. These investigations enabled to propose the electronic mechanism of these reactions. Similarly the electrical conductivity of zinc oxide was examined in dependence on pressure and the composition of surrounding atmosphere. On this basis a band model for the oxygen sorption on this compound was proposed. Analogical works were carried out with nickel and tungsten oxides /Haber and Dereń - Cracow/.

Investigations carried out in Wrocław had the purpose to recognize the influence of a carrier on the electronic structure of the paramagnetic metal deposited on it /for instance palladium/, what can be followed by measuring the magnetic susceptibility. It has been stated that paramagnetism of deposited metals, even at lowest concentrations does not change in an abnormal way. Instead, there exists an effect of the support or carrier on the electronic structure of metal, connected with the interface between the semiconductor and metal, or sometimes with the chemical interaction. Thus, there exist some possibilities to explain the differences in catalytic effectiveness of the same metal in dependence on the applied carrier. A magnetic method of determination of the dispersion degree of metals on the carrier was elaborated as well.

In heterogenous catalysis besides the electronic factor also the sorption and diffusion processes and the capillary structure of the contact are of essential importance, particularly in respect of its utilisation in technological processes. These problems of catalysis were investigated by prof. Sokalski and his co-workers /Gliwice/.

To the theoretical aspects of catalysis belongs a mathematical approach to formulation of the relations between distribution coefficient of active areas on the catalyst surface on the one hand, and the activation energy of adsorption and activity of the contact on the other, these speculations having been made on the example of iron contacts.

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Some further researches dealt with the characteristics of the carriers, especially in respect to the structure of silica, diffusion processes and calculations of effective porosity.

Further important work dealing with catalysis rather from technological point of view has been made by the Branch Institutes of General Chemistry /E.Treszczanowicz - Warsaw/ and of Organic Synthesis, but this is beyond the limits of this lecture.

Sorption processes are not only essential in the catalysis but also in sorbent applications, e.g. in dehydration or decolouration processes which have been the subject of further researches. An attempt to generalise the Szyszkowski's equation by applying Hüttig-Fergusson's and Barrer's isotherms and the discussion of its characteristic points was given by M.Lason /Cracow/. The sorption properties of alumina and silica gels were investigated by Bielański by measurements of the sorption of water vapour. He found that irreversible sorption depends first of all on the calcination temperature while the physically reversible one depends on the capillary structure being connected with preparation mode of the sorbent itself. The activity of alumina gels was examined by W.Kuczyński /Poznań/ and that of silica gel by F.Pollak /Cracow/, a dynamical method being applied by the latter. A competitive method in respect to BET was elaborated by L.Czerski /Cracow/ in application to the bituminous coal by the absorption of p-cresole from aqueous solution. In different way there are explained and characterised the activity and sorption properties of the surface of metallic powders and coal. Prof.Tomassi /Warsaw/ applied here potentiometric measurements, using powder electrodes designed by himself, giving at the same time the mechanism of establishing of the potentials on the said electrodes; these potentials change with catalytical activity. He formulated as well a simple functional dependence for the carbon-powder electrode.

My present statement on the development of physico-chemical sciences may be considered to be completed. I would

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like to add still some ideas about the youngest branch in this country, i.e. the nuclear chemistry. Well, the development of nuclear chemistry has been initiated since the creation of the Institute of Nuclear Research and because of a particular attention paid to this branch by the authorities. On the field of stable isotopes which have been the subject of prof. Zlotowski's /Warsaw/ investigations it should be mentioned here the improved by him method of "dripping drops" for determination of heavy water contents and examining of isotopic effect at moist combustions of some organic substances, as well as the investigations on the characteristics of GM counters for determination of C^{14} in gaseous phase. A. Dorabialska /Łódź/ continued her investigations on the weak radioactivity of some chemical elements and initiated further researches on the application of radioisotopes to study surface phenomena.

In the Institute of Nuclear Research they worked on the preparation of marked compounds like barium hypophosphate $/P^{32}/$, sodium cyanide $/C^{14}/$ and sulphur dioxide $/S^{35}/$ both in water solutions and on carrier. As well they succeeded in obtaining from sulphur a carrier-free phosphorus P^{32} . Prof. Campbell's investigations followed two directions: in the branch of hot atoms chemistry he observed the chemical effects of neutrons on triethylphosphate, using for the first time preparations additionally marked with P^{32} what enabled a better identification of the reaction products; on the other hand he followed the chemical effects of isomeric conversion of Br^{80} using bromide ions what brought about a break of Br-O bonds and formation of bromides, since the repulsion energy of bromine atom well exceeds the value of the tenth ionisation potential. While irradiating with neutrons the arsenious chloride in benzene they stated a formation of arseno-phenyl compounds through phenyl radicals. Further works concerned the mechanism of deposition of trace quantities of radioactive cations like those of Sr, Ce and Co on metallic surfaces. This mechanism does not follow the simple rules resulting from the standart potentials, but is essential for the knowledge of conta-

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mination processes on metallic surfaces by radioelements. Finally it should be mentioned that some researches on the plutonium chemistry and also the radiation chemistry have been commenced.

Such is the general picture of the development of physical and inorganic chemistry within the last 15 years. Realizing that for the first five years of that period we were endeavouring to overcome the disastrous consequences of the war, to restore and equip our laboratories as well as to fulfil immense didactic duties, the picture presented here concerns in fact the last ten years, what is also evident from the small number of papers published till 1949, which amounts only 8% of the total. The development of chemical sciences was here presented on the basis of works having been already published, but it should be completed by numerous works being announced for the present Congress and which could not have been spoken about. There must also be added a series of valuable monographs on different problems of physical chemistry that have been published hitherto.

The review of our achievements exposed their positive and in some instances negative aspects. It is evident where, to what an extent and in what a range the traditional and new branches of chemistry are developed in this country and what the results are like. The general conclusion that may be drawn allows to consider the balance of the physical chemistry branches in question to be positive. Zealous and continuous efforts brought about not only the restoration of chemical sciences but also their development to a much larger extent than in the inter-war period, what is in agreement with the general situation in this country in any respect.

Now let me raise a question: what perspectives of these branches of chemistry may be expected and desired for the future?

I think that there exist conditions necessary for a successful development of investigations on the structure in general, connected with chemical and physical theories. A cooperation between experimental chemists and theoreticians closer than hitherto, would be welcomed.

The researches on phase equilibria should get wider experimental base including new methods, thus enabling to extend the temperature and pressure ranges, and then the theoretical interpretation.

Interface phenomena are closely related to technological processes being of such importance as the flotation and catalysis. Further development in these branches would be most desirable and in the case of catalysis the researches in kinetics should be extended.

A broader than hitherto treatment of the colloid chemistry seems to be a necessity, and the creation of a new Chair would be most advisable in due time.

The branch of physical chemistry of large-molecule substances is undeveloped despite of its close connection with synthetic resins and biochemistry.

In all the mentioned branches the application of stable and radioactive isotopes should be broader than hitherto.

Our share in the world chemistry is not large. In view of expected eminent development of chemical researches in the world the preservation of our actual position, or its improvement, will require a serious effort. However, it is possible to intensify the development of this or that particular branch of chemistry by concentrating our efforts and thus to come ahead though in one narrow section. But planning in science is entirely different than that in industry because here the human factor and its individual ability comes forward, being not subordinated to suggested forms. Therefore the development of chemical sciences in Poland will depend in the first place on further personal creative capacity of scientists, their conceptual and organizing abilities, and this point of view is proved by the development of chemistry in such countries like Switzerland or Sweden.

It must be clearly realized that the development of some particular branches of chemistry will be conditioned by proper research workers, or even better whole teams of clever, inventive people, who would and could overcome the difficulties, people being ceased by overwhelming passion to discover

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new facts and new rules.

I wished that there were many such a people among us, particularly among the younger chemists, because they are to follow the new routes of development of chemistry. Let them successfully develop this science so that in the next ten years before the fiftith Jubilee of our Chemical Society the achievements of the Polish chemistry be expressed by most serious results as well for the sake of science, as to the advantage of our society and all peace-loving nations.-